

Synthesis and characterization of a novel photosensitive triazene polymer

Jürgen Stebani, Oskar Nuyken*

Lehrstuhl für Makromolekulare Chemie I, Universität Bayreuth, 8580 Bayreuth, Germany^{a)}

Thomas Lippert, Alexander Wokaun

Lehrstuhl für Physikalische Chemie II, Universität Bayreuth, 8580 Bayreuth, Germany

(Received: February 16, 1993; revised manuscript of March 9, 1993)

Introduction

Triazene compounds have recently attracted attention due to a variety of interesting properties. The cytostatic activity discovered for several substituted triazenes^{1,2)} has stimulated intense research efforts directed towards the development of triazene-based drugs³⁾. In view of the importance of this field, several reviews on the synthesis of triazenes are available^{4–7)}. A second class of applications is based on the fact that the triazeno group is comparatively stable with respect to thermal decomposition, but undergoes facile photo-chemical cleavage releasing nitrogen. This property, which may lead to novel applications in photolithography and photoreproduction, is the motivation for the present study.

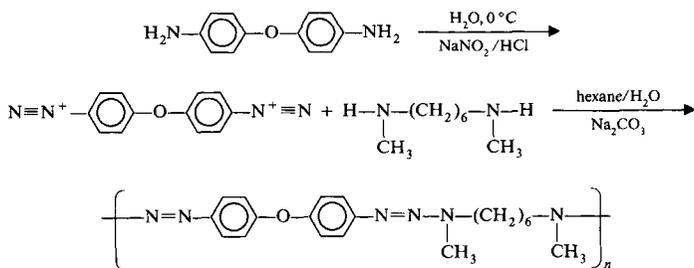
Photopolymers which can be structured by light are important materials in the microelectronics industry. Laser ablation of polymers^{8,9)} has been intensively investigated in this context; the laser treatment represents a dry processing technique, without the need for wet processing steps. Powerful XeCl*-excimer lasers emitting at 308 nm are available for reliable large-scale industrial operation, making it desirable to use this wavelength in polymer ablation. However, many polymers suitable for application in microelectronics do not absorb at this wavelength.

Therefore, progress has been made recently in sensitizing these polymers for ablation at 308 nm, by the addition of low-molecular-weight chromophors. Acridine¹⁰⁾, benzophenone¹¹⁾, pyrene¹²⁾, porphyrines¹³⁾ and 1,3-diphenyltriazenes^{14,15)} have been tested for this purpose. Recently, we have successfully used and characterized several 1-phenyl-3,3-dialkyltriazenes as dopants for the ablation of poly(methyl methacrylate) (PMMA) at 308 nm¹⁶⁾.

An attractive alternative to physical doping is the incorporation of the triazeno group into the polymer itself. Recently, polymer-analogous reactions have been used to synthesize a PMMA copolymer containing ca. 0,3 mol-% of triazene side chains¹⁷⁾.

In the present communication, we are investigating the synthesis of another novel type of photopolymer which contains two triazeno groups per repeating unit. Synthesis is carried out by a polycondensation reaction in which a bis-diazonium salt and a

^{a)} New address: Lehrstuhl für Makromolekulare Stoffe, TU München, Lichtenbergstr. 4, D-8046 Garching, Germany.



bifunctional secondary aliphatic amine react in an interfacial polycondensation yielding a polymer which contains the photosensitive triazene group in the polymer backbone.

Results and discussion

The bis-diazonium salt used in the present investigation was synthesized by the well-known diazotation reaction of an aromatic amine with sodium nitrite in aqueous acidic solution. The diazonium salt solution was reacted under interfacial polycondensation conditions with the aliphatic amine dissolved in a water-immiscible solvent, like it is shown in the following scheme, yielding a high-molecular-weight triazene polymer (Fig. 1).

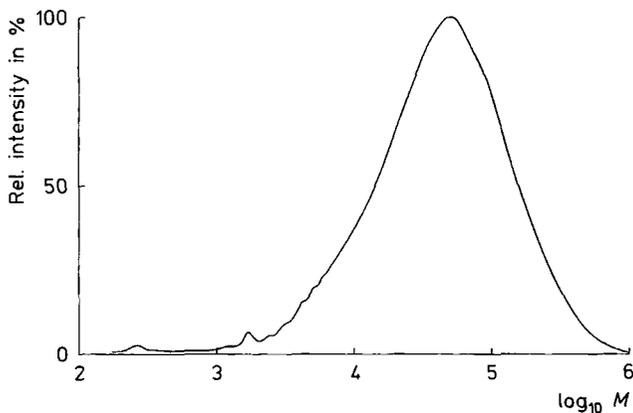


Fig. 1. Gel permeation chromatogram of the triazene group containing polymer synthesized by interfacial polycondensation

The gel permeation chromatography (GPC) of this triazene polymer was calibrated with PMMA-standards. Although this calibration may give rise to a systematic

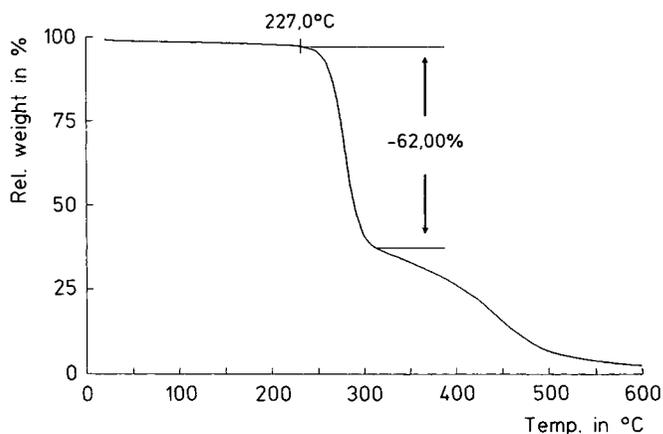


Fig. 2. TGA curve of the triazene polymer measured at a heating rate of 10 K/min

deviation from the correct molecular mass it is a strong indication that high molecular masses in the range of $\bar{M}_n = 15\,000 \text{ g} \cdot \text{mol}^{-1}$ can be reached quite easily. This interpretation is supported by the absence of oligomer peaks in the GPC of this triazene polymer.

The polymer has a UV absorption maximum at 332 nm, with a molar absorption coefficient of $33\,000 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, (for the repeating unit) and shows a decomposition temperature higher than 220 °C in differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). A thermogravimetric measurement is shown in Fig. 2.

According to the proposed mechanism of the thermal decomposition of bis-triazenes¹⁸⁾ the triazene polymer decomposes to form σ -radical species. Provided that the radical species are non-volatile, the triazene polymer should exhibit weight loss at the decomposition temperature not exceeding the stoichiometric amounts of 1,6-bis(methylamino)hexane and nitrogen. At temperatures higher than 300 °C the TGA measurement shows a weight loss resulting from the aromatic species formed during thermal decomposition. On the basis of these assumptions, the calculated weight loss should be 54%. The observed weight loss of 62% is very close to the calculated value.

Studies of pattern formation in films of the triazene polymer by excimer laser irradiation have been performed. Well defined structuring of the polymer surface has been observed, as discussed in detail elsewhere¹⁹⁾.

In conclusion, a novel photosensitive polymer possessing triazene units in the main chain was successfully synthesized by interfacial polycondensation yielding a high-molecular-weight polymer. The very well soluble triazene polymer affords transparent, light yellow films by simple spin-coating and solution-casting techniques and hence represents a thermally stable, highly photosensitive material for use in laser-structuring in microlithography techniques.

Experimental part

Materials

Bis(4-aminophenyl) ether was recrystallized three times from water, and 1,6-bis(methylamino)-hexane was freshly distilled before use. All reactions were carried out in a darkened laboratory.

Polymerization

The polymer was synthesized by interfacial polycondensation. 2,00 g (0,01 mol) of bis(4-aminophenyl) ether was dissolved in 20 mL of 10% hydrochloric acid. The mixture was cooled to -5°C in a dry ice/acetone bath, a cooled solution of 1,38 g (0,02 mol) of sodium nitrite in 5 mL of distilled water was added dropwise, and the reaction mixture was stirred for five minutes. The resulting bis-diazonium salt solution is treated with a cooled solution of 10,0 g of sodium carbonate in 50 mL of distilled water. With vigorous stirring, a solution of 1,44 g (0,01 mol) of 1,6-bis(methylamino)hexane in 50 mL of hexane is added to the reaction mixture. The polycondensation is completed after 15 min. The light beige product is filtered off, washed with water and hexane, dissolved in tetrahydrofuran (THF), precipitated in methanol, and dried in vacuo over diphosphorus pentoxide. Yield 83%.

Characterization of the product

^1H NMR (in dimethyl sulfoxide- d_6): $\delta = 1,2-1,4$ (m; 4H), 1,5-1,8 (m; 4H), 3,0-3,2 (s; 6H), 3,6-3,8 (t; 4H), 6,8-7,4 (m; 8H).

FTIR (in KBr pellet): 2926 (CH_2), 1492, 1354, 1234 cm^{-1} .

UV/Vis (in THF): $\lambda_{\text{max}} = 332$ nm; $\epsilon = 33\,000$ $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$.

DSC: $T_{\text{G}} = 68^{\circ}\text{C}$; maximum of decomposition $T_{\text{dec}} = 276^{\circ}\text{C}$.

TGA: begin of weight loss at 227°C .

GPC: $\bar{M}_{\text{n}} = 15\,000$ g/mol; $\bar{M}_{\text{w}} = 71\,000$ g/mol (PMMA-standard); in THF as solvent.

Measurements

IR spectra were recorded on a Biorad Digilab FTS-40 Fourier transform spectrometer, and UV/Vis-spectra were registered on a Hitachi U-3000 spectrometer. NMR spectra were obtained on a Bruker AC 250. Differential scanning calorimetry (DSC) and thermogravimetry (TGA) measurements were performed at a heating rate of 10 K/min. For DSC measurements a Perkin-Elmer DSC 7 was used, TGA measurements were carried out on a Netzsch STA 409.

- 1) T. Giraldi, T. A. Connors, G. Carter, Eds., "Triazines - Chemical, Biological and Clinical Aspects", Plenum Press, New York 1990
- 2) D. E. V. Wilman, *Magn. Reson. Chem.* **28**, 729 (1990)
- 3) B. J. Foster, D. R. Newell, J. Carmichael, A. L. Harris, L. A. Grumbell, *Br. J. Cancer* **58**, 276 (1988)
- 4) C. Stilling, in "Houben-Weyl", 4th edition, vol. 10/3, Georg-Thieme-Verlag, Stuttgart 1964, p. 699 ff.
- 5) A. Engel, in "Houben-Weyl", 4th edition, vol. E 16a/2, Georg-Thieme-Verlag, Stuttgart 1990, p. 1183 ff.
- 6) P. A. S. Smith, "The Chemistry of open-chain organic nitrogen compounds", vol. II, W. A. Benjamin, Inc., New York 1966, p. 333 ff.
- 7) F. R. Benson, "The High Nitrogen Compounds", Wiley, New York 1984

- 8) R. Srinivasan, B. Braren, *Chem. Rev.* **89**, 1303 (1989)
- 9) S. Lasare, V. Gravier, *Laser Chem.* **10**, 25 (1989)
- 10) R. Srinivasan, B. Braren, R. W. Dreyfus, L. Hachl, D. E. Seeger, *J. Opt. Soc. Am.* **B3**, 785 (1986)
- 11) H. Masuhara, H. Hiraoka, K. Damers, *Macromolecules* **20**, 450 (1987)
- 12) H. Hiraoka, T. J. Chuang, H. Masuhara, *J. Vac. Sci. Technol.* **B6**, 463 (1988)
- 13) H. Fukumura, N. Mibuka, S. Eura, H. Masuhara, *Appl. Phys.* **A53**, 255 (1991)
- 14) M. Bolle, K. Luther, J. Troe, J. Ihlemann, H. Gerhardt, *Appl. Surf. Sci.* **46**, 279 (1990)
- 15) J. Ihlemann, M. Bolle, K. Luther, J. Troe, *Proc. SPIE-Int. Soc. Opt. Eng.* **1361**, 1011 (1990)
- 16) T. Lippert, A. Wokaun, J. Stebani, O. Nuyken, J. Ihlemann, *Adv. Mater. Opt. Electron.*, submitted
- 17) T. Lippert, A. Wokaun, J. Stebani, O. Nuyken, J. Ihlemann, *Angew. Makromol. Chem.* **206**, 97 (1993)
- 18) A. N. K. Lau, L. P. Vo, *Macromolecules* **25**, 7294 (1992)
- 19) T. Lippert, A. Wokaun, J. Stebani, O. Nuyken, J. Ihlemann, *Adv. Mater.*, submitted